

PATENT SPECIFICATION
NO DRAWINGS

1,100,827

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Index at acceptance:—C3 R(22C1, 22C6A1, 22C9B, 22C9N, 22C9Q, 22C11, 22C12, 22C13P, 22C13S, 22C14A, 22C19, 22C22, 22C24, 22C25, 22C29, 22D3C, 22G, 22L1A, 22L1B, 22L2X, 22L6A, 22L6D, 22L6G, 22N1A, 22NX, 22PX, 22T2); B2 E(E1A, E1C, E1H); B2 K(2B, 2E, 2Y, 4A, 4D, 7A1, 7A2, 7A3, 7AX, 7AY, 7B5, 8A, 8D, 9H, 9M, 9Q1, 9Q3, 9Q4, 9Q5, 9Q6, 9Q11, 9QY); B5 N(17X, 17Y, 19Y, 20X, 20Y, 22X, 24Y, 42X, 45X, 55Y, 170, 172, 177, 184, 188, 191, 195, 214, 220, 222, 227, 234, 238, 241, 245, 250, 280Y, 281Y, 282Y, 283Y, 284Y, 285Y, 290Y, 291Y, 297X, 297Y, 309X, 309Y, 312, 313, 315, 344, 346, 371, 373, 423, 424, 428, 436, 437, 438, 526, 543, 547, 548, 561, 570, 598, 607, 634, 729, 754, 769, 787, 788, 789, 797); C3 C(1B1, 1B2, 1B3, 1E1, 1E2).

Int. Cl.:—C 08 g 33/02

COMPLETE SPECIFICATION

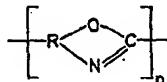
New Polybenzoxazoles, their Production, and Articles
Comprising them

We, E. I. DU PONT DE NEMOURS & COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of Wilmington 98,

5 Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

THIS INVENTION relates to new polybenzoxazoles, their production, and articles comprising them.

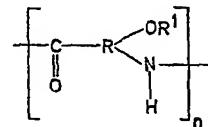
10 The polybenzoxazoles of this invention have the structural formula:



20 wherein R is an aromatic trivalent radical, the nitrogen and oxygen atoms are both attached directly to ring carbon atoms thereof in *ortho* or *peri* positions relative to each other, and the carbon atom shown in the above formula is attached directly to a ring carbon atom of another aromatic trivalent radical R, and n is an integer sufficiently high to provide an inherent viscosity of at least 0.1 (measured at 30°C. as a 0.5% solution in sulphuric acid).

Preferably the intrinsic viscosity is 0.3 to 5.0.

These polybenzoxazoles can be made by a cyclisation reaction, by heating to a temperature of 250°—500°C., preferably 300°—450°C., and for a time sufficient to effect the cyclisation, a polyamide (which will usually be in the form of a shaped article or composition, e.g. a coating), having the structural formula:



wherein R is an aromatic trivalent radical and the carbon, nitrogen and oxygen atoms are each attached directly to ring carbon atoms thereof, the nitrogen and oxygen atoms being in *ortho* or *peri*-position relative to each other, —R¹ is hydrogen, —R², —C(=O)R²

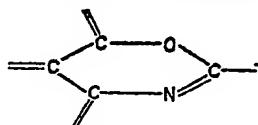
or —C(=O)R³, R² being alkyl of 1—6 carbon

atoms and n is an integer sufficiently high to provide an inherent viscosity of at least 0.1. These polyamides are the subject of our Specification No. 51,265/64 (Serial No.

1,100,826) which may be referred to for a description of their production and conversion into shaped articles and compositions, as well as for information about particular polyamides which can be cyclised to give the polybenzoxazoles of the present invention.

Usually the polyamide will be heated for an hour or more to complete the cyclisation.

The new polybenzoxazoles have outstanding chemical and physical properties, which make them extremely useful in the form of shaped structures such as films, filaments and tubing. They are very compact polymers, in that each polymer unit consists simply of an aromatic nucleus and an oxazole ring, the two adjacent carbon atoms of the oxazole ring being also members of the aromatic nucleus (i.e. in fused ring relationship), and the other oxazole ring carbon being bonded directly to the aromatic nucleus of the next polymer unit. The aromatic nucleus can be mono- or polycyclic, and in the latter case may comprise fused rings as in naphthalene. When the $-\text{OR}$ and $-\text{NH}_2$ groups in the polyamides from which the polybenzoxazoles are formed are in the *peri* positions, the heterocyclic ring is an oxazoline ring



The polybenzoxazoles of this invention find many applications in a wide variety of physical shapes and forms, especially as films and fibres which not only possess excellent physical properties at room temperature, but retain their strength at elevated temperatures for prolonged periods of time. Owing to their solubility, the polyamide precursors can be formed into shaped articles such as films, fibres, tubes, rods, sheets and discs by conventional techniques, and then converted by the above described cyclisation reaction into the final high-melting, relatively intractable polybenzoxazoles of the invention.

The final shaped article may consist of the polybenzoxazole alone or blended with other polymers and/or modified with inert materials. Depending on their nature, such inert materials may be added before or after shaping the polyamide. For example, fillers such as pigments, electrically conductive carbon black and metal particles, abrasives, dielectrics and lubricating polymers may be added conveniently to the intermediate polyamide as such or to a solution of the polyamide before shaping. On the other hand certain abrasives and electrically conductive materials are better added as surface layers after shaping. A cellular form or foam of the polybenzoxazole may be produced by adding a conventional blowing agent to the polyamide, either alone or in combination with

a filler, foaming taking place when the article is heated to form the polybenzoxazole. Alternatively, cellular products can be made by dispersing bubbles (e.g. of air, carbon dioxide, or nitrogen) into a melt or solution of the intermediate polyamide before shaping and cyclisation.

The polyamide intermediate may be in the form of a layer on a substrate, giving for example a coating or an adhesive layer of the polybenzoxazole. Substrates on which such layers can be formed include copper, brass, aluminium, steel, and other metals in the form of sheets, fibres, wires and screening; mineral structures such as asbestos; glass in the form of sheets, fibres, foams and fabrics; polymeric materials such as cellulosic materials (for example regenerated cellulose film, or wood or paper), polyolefines (e.g. polyethylene, polypropylene and polystyrene), polyesters (e.g. polyethylene terephthalate), other polyamides, polyimides, perfluorocarbon polymers (e.g. polytetrafluoroethylene and copolymers of tetrafluoroethylene with hexafluoropropylene) or polyurethanes, all in the form of, for example, sheets, fibres, foams, woven or non-woven fabrics or screening; and leather sheets. The polymeric substrates can be metallized before coating, or treated with a conventional adhesive or other agent to improve surface receptivity. The same substrate materials may be used as top layers over the previously-coated substrates to provide laminates wherein the polybenzoxazole serves as an adhesive layer. Films of the polybenzoxazoles can be laminated to any of the above substrates, in many cases with the aid of a commercially available adhesive.

Films of the polybenzoxazoles of the invention may be used advantageously in wrapping, packaging and bundling applications, in automobile and aviation interior head lining materials, decorative trim, high temperature electrical insulation, in the form of corrosion-resistant pipe, duct work, containers and container linings, and in the laminating structures mentioned previously. In fibre form, the polybenzoxazoles of the invention are useful for high temperature electrical insulation, protective clothing and curtains, filtration media, packing and gusseting materials, brake linings and clutch facings. The combination of thermal and hydrolytic stabilities make articles of the new polybenzoxazoles useful in high temperature steam systems, e.g. steam turbines.

The invention is illustrated by the following Examples.

EXAMPLE 1

A film of an *o*-hydroxypolybenzamide obtained as described in Example 1 of Specification No. 51,265/64 (Serial No. 1,100,826) is heated *in vacuo* at 350°—450°C. until the polyamide has been converted into the cor-

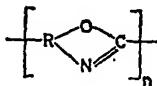
responding polybenzoxazole of inherent viscosity 0.43 determined at 30°C. on a 0.5% solution in sulphuric acid. The film obtained has excellent thermal stability, losing less than 5 1% of its weight during a 3 hour exposure to air at 450°C. or a 4 hour exposure to helium at 500°C.

EXAMPLES 2—21

10 Films of the polyamides of Examples 2—21 of Specification No. 51,265/64 (Serial No. 1,100,826) were treated as in Example 1 above to convert them into the corresponding polybenzoxazoles, whose properties were generally similar to those of the product of 15 Example 1.

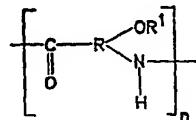
WHAT WE CLAIM IS:—

1. Polybenzoxazoles having the structural formula:



20 wherein R is an aromatic trivalent radical and the nitrogen and oxygen atoms are both attached directly to ring carbon atoms thereof in the *ortho* or *peri* positions relative to each other, and the carbon atom shown in the above formula is attached directly to a ring carbon atom of another aromatic trivalent radical R, and n is an integer sufficiently high to provide an inherent viscosity of at least 0.1 (measured at 30°C. as a 0.5% solution in sulphuric acid).
 25 2. Polybenzoxazoles according to claim 1, having an inherent viscosity of 0.3—5.0.
 3. Polybenzoxazoles according to claim 1 or 2, in the form of shaped articles or coatings.
 30 4. Polybenzoxazoles according to claim 1 substantially as described in the foregoing Examples.
 5. Self-supporting films comprising as at 35 least the principle film-forming component a polybenzoxazole claimed in any one of claims 1—4.
 40 6. process for the production of a poly-

benzoxazole claimed in any one of claims 1—4, which comprises heating to a temperature of 250—500°C., and for a time sufficient to effect the cyclisation a polyamide having the structural formula:



wherein R is an aromatic trivalent radical and the carbon, nitrogen and oxygen atoms are each attached directly to ring carbon atoms thereof, the nitrogen and oxygen atoms being in *ortho*- or *peri*-positions relative to each other, —R¹ is hydrogen, —R², —C(=O)R² or 55

—C(=S)R², R² being alkyl of 1—6 carbon

atoms and n is an integer sufficiently high to provide an inherent viscosity of at least 0.1.

7. Process according to claim 6, wherein the polyamide is heated to 300°—450°C.

8. Process according to claim 6 or 7, wherein in the polyamide is in the form of a self-supporting film.

9. Process according to claim 6 or 7, wherein the polyamide is in the form of a coating or layer on a substrate.

10. Process for the production of a polybenzoxazole according to claim 6 substantially as hereinbefore described.

11. Films and other shaped articles, obtained by a process claimed in any one of claims 6—8 and 10, and coated or laminated articles in which the coating or at least one layer is obtained by a process claimed in any one of claims 6, 7 and 9.

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Reference has been directed in pursuance of Section 9, subsection (1) of the Patents Act, 1949, to patent No. 1,008,854.

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